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Dated 18 August 2005

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~~DUPLICATE~~EXHAUST SYSTEM FOR A DIESEL ENGINE COMPRISING A NO<sub>x</sub>-TRAP

5 The present invention relates to an exhaust system for a diesel engine, which system comprising a first nitrogen oxide (NO<sub>x</sub>)-trap comprising at least one first NO<sub>x</sub> absorbent and platinum.

10 A NO<sub>x</sub>-trap is purposely designed for absorbing and storing NO<sub>x</sub> in lean exhaust gases ( $\lambda > 1$  conditions), and releasing and catalytically reducing the stored NO<sub>x</sub> in rich exhaust gases ( $1 > \lambda$  conditions). To remove the stored NO<sub>x</sub>, typically the engine is controlled so that periodically it is run rich during normal lean-running operation. A NO<sub>x</sub>-trap typically includes active materials for three functions: an oxidation catalyst, such as platinum; an absorbent, for example an alkali metal e.g. a potassium and/or a caesium compound or an alkaline earth compound typified by barium oxide; and a reduction catalyst, such as rhodium. In the exhaust gas the or each alkali metal and alkaline earth metal compound is present as an oxide, although it may also be present in use as a hydroxide or a carbonate.

15 The convention used herein is to refer to a "NO<sub>x</sub>-trap" as a composition comprising a NO<sub>x</sub> absorbent and at least one catalytic material, such as a platinum group metal. NO<sub>x</sub> absorbent refers to the e.g. alkaline earth metal compound or alkali metal compound capable of absorbing nitrogen dioxide (NO<sub>2</sub>) in lean exhaust gas.

An oxidation catalyst is purposely designed to provide for the reaction of gaseous components with oxygen, typically in as wide a temperature range as possible, especially at lower temperatures. The catalyst oxidises whenever oxygen is available for reaction in the gas stream. Active components of an oxidation catalyst can include platinum, palladium or a base metal active for oxidation such as manganese, copper, molybdenum, cobalt or any other transition element that is active for oxidation.

20 An oxygen storage component (OSC) is purposely designed to absorb oxygen from lean exhaust gases and to release oxygen in rich exhaust gas conditions. Examples of suitable OSC include ceria doped with transition metals, e.g. zirconium, or other rare earth metals and manganese-based materials.

Our WO 02/18753 (incorporated herein by reference) describes an exhaust system for a lean-burn internal combustion engine, including a diesel engine, comprising an oxidation catalyst upstream of a NO<sub>x</sub>-trap for oxidising relatively large amounts of unburnt hydrocarbons present in exhaust gas in normal lean-running conditions and for 5 oxidising NO in the exhaust gas to NO<sub>2</sub> in lean-running conditions. In one embodiment, a clean-up catalyst comprising an oxygen storage component such as ceria, an oxidation component, such as platinum, a NO<sub>x</sub> reducing component, for example rhodium, and a component for suppressing H<sub>2</sub>S, for example NiO, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, CoO and CrO<sub>2</sub>, is disposed downstream of the NO<sub>x</sub>-trap.

10 At low exhaust gas temperatures, e.g. about 200-250°C, and part-load, a modern Diesel engine produces a relatively high amount of NO<sub>x</sub> in the form of NO<sub>2</sub>. If, as is typical in an exhaust system for a lean-burn internal combustion engine including a NO<sub>x</sub>-trap, the exhaust gas is first passed over a platinum oxidation catalyst, the NO<sub>2</sub> can be removed by facile low temperature oxidation of hydrocarbons present in the exhaust 15 gas. This process is known as lean NO<sub>x</sub> catalysis. In any event, the NO<sub>x</sub> absorbent material can poison the lean NO<sub>x</sub> activity of the platinum, thereby reducing the conversion efficiency of the process. At higher temperatures, e.g. above about 300-350°C, the oxidation of NO to NO<sub>2</sub> becomes sufficiently rapid for significant quantities of NO<sub>2</sub> to be formed and a conventional platinum containing NO<sub>x</sub>-trap then 20 starts to become effective.

We have now found that by using a NO<sub>x</sub>-absorbent which is free of platinum upstream of a NO<sub>x</sub>-trap comprising platinum to absorb engine-derived NO<sub>2</sub>, the exhaust system as a whole is able to treat NO<sub>x</sub> more efficiently. More particularly, we have found that the system slips less NO<sub>2</sub> to atmosphere than a system comprising a conventional 25 NO<sub>x</sub>-trap comprising a NO<sub>x</sub> absorbent and platinum as the sole NO<sub>x</sub> absorbent-containing component.

According to one aspect, the invention provides an exhaust system for a diesel engine, which system comprising a first NO<sub>x</sub>-trap comprising at least one first NO<sub>x</sub> absorbent and platinum, characterised in that at least one second NO<sub>x</sub> absorbent is disposed upstream of the first NO<sub>x</sub>-trap, which at least one second NO<sub>x</sub> absorbent is not 30 associated with platinum.

An advantage of this system over the above-mentioned prior art system is that the system of the invention generates less N<sub>2</sub>O by lean NO<sub>x</sub> catalysis over the platinum component of the first NO<sub>x</sub>-trap.

The at least one second NO<sub>x</sub>-absorbent can be associated with a base metal catalyst for oxidising nitrogen monoxide (NO) to nitrogen dioxide (NO<sub>2</sub>) in lean exhaust gas or a non-platinum platinum group metal, such as rhodium or iridium, for reducing NO<sub>x</sub> to N<sub>2</sub> in rich exhaust gas.

According to a further aspect, the invention provides an exhaust system for a diesel engine, which system comprising a first NO<sub>x</sub>-trap comprising at least one first NO<sub>x</sub> absorbent and platinum, characterised in that a second NO<sub>x</sub>-trap is disposed upstream of the first NO<sub>x</sub>-trap, which second NO<sub>x</sub>-trap comprising at least one second NO<sub>x</sub> absorbent and at least one platinum group metal selected from the group consisting of rhodium, palladium, iridium, osmium and ruthenium.

15

The first NO<sub>x</sub>-trap can be coated on a flow-through monolith, but in one embodiment, it is coated on a particulate filter. In a further embodiment according to the latter aspect, the particulate filter can include a diesel oxidation catalyst, optionally comprising supported platinum and/or palladium.

20

Optionally there may be a catalyst for oxidising NO to NO<sub>2</sub>, such as platinum on an alumina support, disposed between the at least one second NO<sub>x</sub> absorbent and the first NO<sub>x</sub>-trap as described in our WO 02/18753.

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During NO<sub>x</sub>-trap regeneration, pulses of rich exhaust gas can be produced by the engine to convert stored NO<sub>x</sub> to nitrogen. During this process, hydrocarbon or carbon monoxide could pass through the system to atmosphere. To prevent this, the gas downstream of the first NO<sub>x</sub>-trap can be passed over an oxidation catalyst comprising an oxygen storage component, so even if the gas is overall reducing, reductants can still be oxidised, and prevented from entering the atmosphere. In one embodiment, the oxidation catalyst comprises platinum or palladium supported on a bulk ceria-zirconia mixed oxide oxygen storage component.

According to a further aspect, the invention provides a diesel engine, optionally a light-duty diesel engine (as defined by the relevant legislation) comprising an exhaust system according to the invention. As is typical for engines including exhaust systems comprising NO<sub>x</sub>-traps, the engine can include an engine control unit (ECU) programmed, 5 in use, to adjust the exhaust gas composition to the rich side for regenerating the at least one first NO<sub>x</sub> absorbent and the at least one second NO<sub>x</sub> absorbent.

According to a further aspect the invention provides a flow through substrate comprising a NO<sub>x</sub>-trap comprising a first zone coated with a composition comprising at 10 least one first NO<sub>x</sub> absorbent and platinum and a second zone coated with a composition comprising at least one second NO<sub>x</sub>-absorbent, which at least one second NO<sub>x</sub> absorbent is not associated with platinum.

According to a further aspect the invention provides a flow-through substrate 15 comprising a first zone comprising a first NO<sub>x</sub>-trap composition comprising at least one first NO<sub>x</sub> absorbent and platinum and a second zone comprising a second NO<sub>x</sub>-trap composition comprising at least one second NO<sub>x</sub>-absorbent and at least one platinum group metal selected from the group consisting of rhodium, palladium, iridium, osmium and ruthenium.

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According to a further aspect, the invention provides a method of treating NO<sub>x</sub> in the exhaust gas of a diesel engine, which method comprising absorbing NO<sub>2</sub> from lean exhaust gas in at least one second NO<sub>x</sub> absorbent; oxidising NO in lean exhaust gas to NO<sub>2</sub> at 300°C and above over a platinum catalyst and absorbing the NO<sub>2</sub> generated from 25 oxidising NO in at least one first NO<sub>x</sub>-absorbent; desorbing the stored NO<sub>x</sub> in rich exhaust gas and reducing the desorbed NO<sub>x</sub> to N<sub>2</sub>.

In order that the invention may be more fully understood, reference is made to the sole accompanying drawing which shows a schematic diagram of a diesel engine 30 comprising an exhaust system according to the invention. It is believed that the Figure, as annotated, is self-explanatory.

CLAIMS:

1. An exhaust system for a diesel engine, which system comprising a first NO<sub>x</sub>-trap comprising at least one first NO<sub>x</sub> absorbent and platinum, characterised in that at least one second NO<sub>x</sub> absorbent is disposed upstream of the first NO<sub>x</sub>-trap, which at least one second NO<sub>x</sub> absorbent is not associated with platinum.  
5
2. An exhaust system according to claim 1, wherein the at least one second NO<sub>x</sub>-absorbent comprises a base metal catalyst for oxidising nitrogen monoxide (NO) to nitrogen dioxide (NO<sub>2</sub>) in lean exhaust gas.  
10
3. ~~An exhaust system according to claim 1 or 2, wherein the at least one second NO<sub>x</sub>-absorbent comprises a non-platinum platinum group metal (PGM) for reducing NO<sub>x</sub> to N<sub>2</sub> in rich exhaust gas.~~  
15
4. An exhaust system according to claim 3, wherein the PGM is rhodium or iridium.
5. An exhaust system for a diesel engine, which system comprising a first NO<sub>x</sub>-trap comprising at least one first NO<sub>x</sub> absorbent and platinum, characterised in that a second NO<sub>x</sub>-trap is disposed upstream of the first NO<sub>x</sub>-trap, which second NO<sub>x</sub>-trap comprising at least one second NO<sub>x</sub> absorbent and at least one platinum group metal selected from the group consisting of rhodium, palladium, iridium, osmium and ruthenium.  
20
6. An exhaust system according to any of claims 1 to 5, wherein the first NO<sub>x</sub>-trap comprises a particulate filter.  
25
7. An exhaust system according to claim 6, wherein the particulate filter also includes a diesel oxidation catalyst, optionally comprising supported platinum and/or palladium.  
30
8. An exhaust system according to any preceding claim, further comprising a catalyst for oxidising NO to NO<sub>2</sub> disposed between the at least one second NO<sub>x</sub> absorbent and the first NO<sub>x</sub>-trap.

9. An exhaust system according to claim 8, wherein the NO oxidation catalyst is platinum on an alumina support.
  10. An exhaust system according to any preceding claim, further comprising a catalyst comprising a catalyst component for oxidising hydrocarbon and carbon monoxide to water and carbon dioxide and an oxygen storage component, which catalyst is disposed downstream of the first NO<sub>x</sub>-trap.
  11. An exhaust system according to claim 10, wherein the oxidation catalyst comprises platinum or palladium supported on a bulk ceria-zirconia mixed oxide oxygen storage component.
- 
12. A diesel engine comprising an exhaust system according to any preceding claim.
  13. A light-duty diesel engine according to claim 12.
  14. An engine according to claim 12 or 13, comprising an engine control unit programmed, in use, to adjust the exhaust gas composition to the rich side for regenerating the at least one first NO<sub>x</sub> absorbent and the at least one second NO<sub>x</sub> absorbent.
  15. A flow-through substrate comprising a NO<sub>x</sub>-trap comprising a first zone coated with a composition comprising at least one first NO<sub>x</sub> absorbent and platinum and a second zone coated with a composition comprising at least one second NO<sub>x</sub>-absorbent, which at least one second NO<sub>x</sub> absorbent is not associated with platinum.
  16. A flow-through substrate comprising a first zone comprising a first NO<sub>x</sub>-trap composition comprising at least one first NO<sub>x</sub> absorbent and platinum and a second zone comprising a second NO<sub>x</sub>-trap composition comprising at least one second NO<sub>x</sub>-absorbent and at least one platinum group metal selected from the group consisting of rhodium, palladium, iridium, osmium and ruthenium.

17. A method of treating NO<sub>x</sub> in the exhaust gas of a diesel engine, which method comprising absorbing NO<sub>2</sub> from lean exhaust gas in at least one second NO<sub>x</sub> absorbent; oxidising NO in lean exhaust gas to NO<sub>2</sub> at 300°C and above over a platinum catalyst and absorbing the NO<sub>2</sub> generated from oxidising NO in at least one first NO<sub>x</sub>-absorbent;  
5 desorbing the stored NO<sub>x</sub> in rich exhaust gas and reducing the desorbed NO<sub>x</sub> to N<sub>2</sub>.
18. An exhaust system substantially as described herein with reference to the accompanying drawing.
- 10 19. An engine substantially as described herein with reference to the accompanying drawing.
- 
20. A method substantially as described herein.

## EXHAUST SYSTEM FOR A DIESEL ENGINE COMPRISING A NO<sub>x</sub>-TRAP

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### Abstract

An exhaust system for a diesel engine comprises a first NO<sub>x</sub>-trap comprising at least one first NO<sub>x</sub> absorbent and platinum, characterised in that at least one second NO<sub>x</sub> absorbent is disposed upstream of the first NO<sub>x</sub>-trap, which at least one second NO<sub>x</sub> absorbent is not associated with platinum.

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[Figure 1]

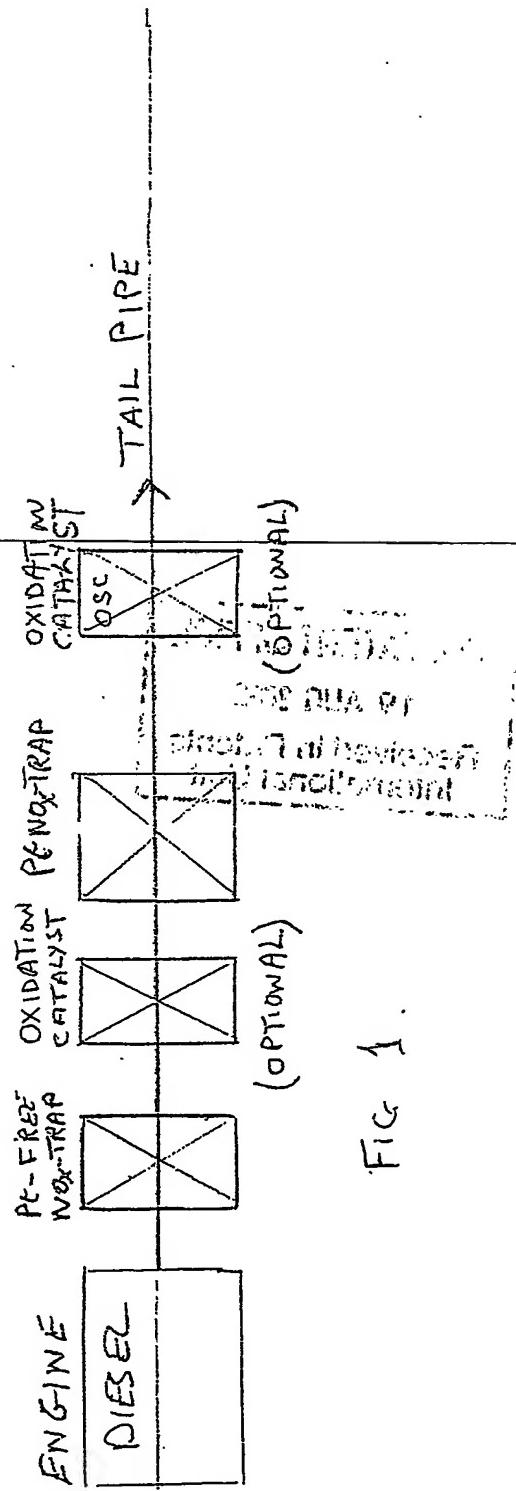


FIG 1.

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